Title of research project : NEW FLUORIDE GLASSES FOR THE PREPARATION OF INFRARED OPTICAL FIBERS

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New indium-based fluoride glasses have been optimized in order to decrease the devitrification rate. A five-component material with the composition 30 BaF_2-30 InF_3-20 ZnF_2-10 YF_3-10 ThF_4 has been selected because of a high difference between crystallization Tx and glass Tg temperatures with a Δ Tx-Tg = 123° C. This glass appears to be the most stable zirconium-free fluoride glass, allowing the preparation of samples with 20 mm thickness.

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FIRST PERIODIC REPORT

A new family of fluoride glasses based on the association of InF_3 and BaF_2 as major elements has been discovered and investigated. These zirconium-free vitreous materials exhibit a broad transmission range from 0.25 in the U.V. to 8 µm in the I.R.

This report described the systematic investigations made to optimize the compositions with the aim of keeping the exceptional transparency and avoiding the devitrification process which is very common with this kind of glasses. Many four-component systems such as BaF_2-InF_3-ThF_4-ZnF_2, BaF_2-InF_3-YbF_3-ZnF_2, BaF_2-InF_3-ThF_4-YbF_3 have been explored by Differential Scanning Calorimetry in order to find a composition with the largest difference between crystallization temperature Tx and glass temperature Tg. In these systems, the maximum Δ Tx-Tg is around 100° C for example for the composition 30 BaF_2-30 InF_3-20 ZnF_2-20 ThF_4 which appears to be one of the best for a four-component glass. From the melt of such composition which has a suitable viscosity around 680° C, it has been possible to obtain large samples with a maximum thickness of 10 mm, without apparent crystallization.

Finally, a five-component composition has been systematically explored in replacing step by step ThF_4 by a rare-earth fluoride such as YF_3 or YbF_3 in the previous optimized materials.

The best glass in term of Δ Tx-Tg maximum is obtained for the composition : 30 BaF_2-30 InF_3-20 ZnF_2-10 YbF_3-10 ThF_4. This glass is called BIZYT and shows a Δ Tx-Tg = 123° C, the highest value never obtained for a Zr-free glass. Consequently samples of 20 to 30 mm thickness have been prepared without apparent crystallization.

The I.R. transmission spectra of such glasses indicate that the multiphonon edge is shifted of about 1-2 µm towards the longer wavelength compared to fluorozirconate glasses.

Precise measurements of the absorption coefficient α versus λ show that the V-shape curve for such materials is giving a potential ultratransparency close to 10^{-3} dB/km near 3 μm. As a reference, the theoretical value of the absorption loss at the CO laser wavelength close to 5.3 μm is estimated around 100 dB/km. For the same λ, the effective loss in the case of fluorozirconate glasses is more than 10^4 dB/km.

This five-component glass BIZYT has also been investigated by calorimetry technics for acceeding to the Time-Temperature-Transformation curves. The best glass with the composition already described has a critical cooling rate of 60° C/minute.

All the samples and characterization measurements have been made in the normal atmospheric conditions. The preparation of the glasses, for instance, is very simple and corresponds to the classical procedure of transforming the metallic oxides in fluoride in using NH_4H,HF as a fluorinating agent at 300° C. Then the fluorides are melted at 800° C, cooled at 700° C and poured on a brass mould.

During the process, some corrosion of the melt by atmospheric humidity is observed due to the formation of white fumes. Therefore, the degree of corrosion of the glass which is measured by the intensity of the OH peak in the bulk is much more weak in this familly of fluoride glasses compared to the fluorozirconates.

The next step of the study which is already started will include the systematic study of the corrosion of bulk samples by liquid water and vapor and the determination of the molar absorption coefficient ε_{OH} in these indium-based glasses. Also the variation of refractive index as a function of chemical composition will be measured and included in the next report. In parallel, we will paid a permanent attention to increase the stability of the glass towards devitrification by small modification of the composition, but in keeping the good transmission properties.

A part of the work will be presented at the IV International Symposium on Halide Glasses at Monterey, California (U.S.A.) in the week 23-27 january 1987.